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U.S. PATENT APPLICATION

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Invention: USE OF 2-(SULPHONYLAMINO) PHENOLS AS COUPLERS IN
OXIDATION COLOURING

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SPECIFICATION

Use of 2-(sulphonylamino)phenols as couplers in
oxidation colouring

5 The invention relates to the field of the oxidation
dyeing of keratinous fibres and in particular of human
keratinous fibres, such as the hair. The invention
relates more particularly to the use of certain
2-(sulphonylamino)phenols in combination with oxidation
dye precursors for the oxidation dyeing of fibres.

10 It is known to dye keratinous fibres and in particular
human hair with dyeing compositions comprising oxidation
dye precursors, in particular para-phenylenediamines,
ortho- or para-aminophenols, or heterocyclic compounds,
15 such as diaminopyrazole derivatives, generally known as
oxidation bases. Oxidation dye precursors or oxidation
bases are colourless or weakly coloured compounds which,
in combination with oxidizing substances, can give rise
by an oxidative coupling process to coloured and
20 colouring compounds.

It is also known that the shades obtained with these
oxidation bases can be varied by combining them with
couplers or colouring modifiers, the latter being chosen
25 in particular from aromatic meta-diamines, meta-
aminophenols, meta-diphenols, non-cationic naphthols or
certain heterocyclic compounds, such as, for example,
indole couplers.

30 The variety of the molecules employed as oxidation bases
and couplers makes it possible to obtain a rich palette
of colours.

The «permanent» colouring obtained by virtue of these oxidation dyes has, however, to satisfy a certain number of requirements. Thus, it must be without disadvantage
5 toxicologically, it must make it possible to obtain shades in the desired intensity and it must behave well in the face of external agents (light, bad weather, washing, permanent waving, perspiration or rubbing).

- 10 The dyes must also make it possible to cover white hair and, finally, be as unselective as possible, that is to say make it possible to obtain the least possible differences in colouring along the same keratinous fibre, this being because the latter can be sensitized (i.e.
15 damaged) to a varying degree between its tip and its root.

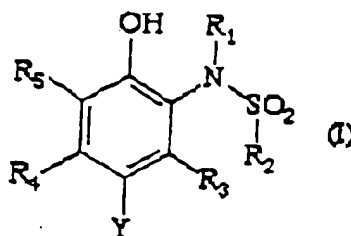
Provision has already been made, in particular in Patent Application BE 803 712, for oxidation dyeing compositions
20 comprising nitrated 2-(sulphonylamino)phenols as direct yellow dye or as yellow couplers, in combination with oxidation bases conventionally used in oxidation dyeing, such as, for example, para-phenylenediamine, para-toluylenediamine, para-dimethylaminoaniline, para-amino-
25 phenol or para-diaminoanisole. Such compositions are not, however, always satisfactory, in particular from the viewpoint of the power and the chromaticity of the colourings obtained.

- 30 The Applicant Company has now just discovered, in a completely unexpected and surprising way, that it is possible to obtain novel dyes, which dyes are capable of

resulting in powerful colourings in shades varying from red to blue which are particularly chromatic and bright, which are not very selective and which exhibit excellent properties of resistance to the various attacks which keratinous fibres may be subjected to, by combining at least one oxidation base and at least one coupler chosen from certain 2-(sulphonylamino)phenols.

A first subject-matter of the invention is therefore a composition for the oxidation dyeing of keratinous fibres and in particular of human keratinous fibres, such as the hair, comprising, in a medium appropriate for the dyeing of the said fibres:

- at least one oxidation base;
- and at least one coupler chosen from the compounds of following formula (I) and/or their addition salts with an



acid:

in which:

- R_1 represents a hydrogen atom or a linear or branched radical comprising from 1 to 15 carbon atoms (it being possible for the branching or branchings to form one or more carbonaceous rings comprising from 3 to 7 ring members) which can comprise one or more double bonds and/or one or more triple bonds (the said double bonds optionally resulting in aromatic groups) and one or more

carbon atoms of which can be replaced by an oxygen,
nitrogen or sulphur atom or by an SO₂ group and the carbon
atoms of which can, independently of one another, be
substituted by one or more halogen atoms, the said R₁
5 radical comprising neither peroxide bonds nor diazo,
nitro and nitroso radicals;

● R₂ represents a hydrogen atom or a linear or branched
radical comprising from 1 to 20 carbon atoms (it being
10 possible for the branching or branchings to form one or
more carbonaceous rings comprising from 3 to 7 ring
members) which can comprise one or more double bonds
and/or one or more triple bonds (the said double bonds
optionally resulting in aromatic groups) and one or more
15 carbon atoms of which can be replaced by an oxygen,
nitrogen or sulphur atom or by an SO₂ group and the carbon
atoms of which can, independently of one another, be
substituted by one or more halogen atoms, the said R₂
radical comprising neither peroxide bonds nor diazo,
20 nitro and nitroso radicals;

● R₃, R₄ and R₅, which are identical or different,
represent a hydrogen or halogen atom or a linear or
branched radical comprising from 1 to 20 carbon atoms (it
25 then being possible for the branching or branchings to
form one or more rings comprising from 3 to 7 ring
members) which can comprise one or more double bonds
and/or one or more triple bonds (the said double bonds
optionally resulting in aromatic groups) and one or more
30 carbon atoms of which can be replaced by an oxygen,
nitrogen or sulphur atom or by an SO₂ group and the carbon
atoms of which can, independently of one another, be

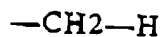
substituted by one or more halogen atoms, the said radical comprising neither peroxide bonds nor diazo, nitro and nitroso radicals and it being understood that R_2 cannot represent a hydroxyl, thio or amino radical and
5 it being understood that the R_1 , R_4 and R_5 radicals cannot be connected to the benzene ring of the formula (I) via an -NH-NH- bond;

• Y represents a hydrogen or halogen atom; an $-OR_6$, $-SR_6$
10 or $-NH-SO_2R_6$ group in which R_6 represents a linear or branched C_1-C_6 alkyl radical (it then being possible for the branching or branchings to form one or more rings comprising from 3 to 6 ring members), optionally substituted by one or more radicals chosen from the group:
15 halogen, hydroxyl, C_1-C_4 alkoxy, amino or C_1-C_4 aminoalkyl; a phenyl radical, optionally substituted by one or two radicals chosen from the group: C_1-C_4 alkyl, trifluoromethyl, carboxyl, C_1-C_4 alkoxy carbonyl, halogen, hydroxyl, C_1-C_4 alkoxy, amino or C_1-C_4 aminoalkyl; or a
20 benzyl radical.

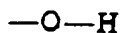
As indicated above, the oxidation dyeing composition comprising the compound or compounds of formula (I) in accordance with the invention makes it possible to obtain
25 powerful colourings in shades varying from red to blue which furthermore exhibit a noteworthy persistence towards the various treatments which keratinous fibres may be subjected to. These properties are particularly noteworthy especially as regards the resistance of the
30 colourings obtained with respect to the action of bad weather, washing, permanent waving and perspiration.

Another subject-matter of the invention is a process for the oxidation dyeing of keratinous fibres employing this dyeing composition.

- 5 According to the invention, when it is indicated that one or more of the carbon atoms of the R_1 to R_5 radical or radicals can be replaced by an oxygen, nitrogen or sulphur atom or by an SO_2 group and/or that the said R_1 to R_5 radicals can comprise one or more double bonds and/or
- 10 one or more triple bonds, this means that it is possible, by way of example, to carry out the following



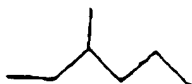
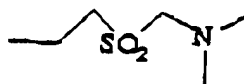
can become



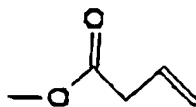
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conversions:

- According to the invention, R_1 preferably denotes a hydrogen atom or an A_1 , A_2 , A_3 , A_4 or A_5 group as defined
- 15 below.

According to the invention, the term « A_1 group» is understood to mean a linear or branched C_1-C_8 hydrocarbonaceous radical which can carry one or two

double bonds or one triple bond, which may or may not be substituted by a group chosen from an A_2 group, an A_1 group or an A_3 group, which may or may not be substituted by one or two identical or different groups chosen from
5 the $N-(C_1-C_3)$ alkylamino, $N-(C_1-C_3)$ alkyl- $N-(C_1-C_3)$ alkylamino, (C_1-C_6) alkoxy, oxo, alkoxycarbonyl, acyloxy, amido, acylamino, ureyl, sulphoxy, sulphonyl, sulphonamido, sulphonylamino, bromo, cyano or carboxyl groups, and which may or may not be substituted by one or more
10 hydroxyl, fluoro or chloro groups.

The term « A_2 group» is understood to mean an aromatic group of phenyl, benzyl or naphthyl type which may or may not be substituted by one to three identical or different
15 groups chosen from the methyl, trifluoromethyl, ethyl, isopropyl, butyl, pentyl, fluoro, chloro, bromo, methoxy, trifluoromethoxy, ethoxy, propyloxy, acetyloxy, acetyl and cyano groups.

20 The term « A_1 group» is understood to mean heteroaromatic groups chosen from the furanyl, thiophenyl, pyrrolyl, imidazolyl, thiazolyl, oxazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, isoxazolyl, isothiazolyl, pyrazolyl, pyrazolotriazolyl, pyrazoloimidazolyl, pyrrolotriazolyl,
25 pyrazolopyrimidyl, pyrazolopyridyl, pyridyl, pyrimidyl, benzimidazolyl, benzoxazolyl, benzothiazolyl, indolyl, indolidinyl, isoindolyl, indazolyl, benzotriazolyl, quinolinyl, benzimidazolyl or benzopyrimidyl groups, optionally substituted by 1 to 3 radicals chosen from
30 linear or branched C_1-C_6 alkyl, C_1-C_6 (poly)hydroxyalkyl, carboxyl, alkoxycarbonyl, halogen, amido, amino or hydroxyl.

The term «A₁ group» is understood to mean a C₃-C₇ cycloalkyl or a norbornanyl radical which can optionally carry a double bond and which is optionally substituted by 1 or 2 radicals defined by linear or branched C₁-C₄ alkyl, C₁-C₄ (poly)hydroxyalkyl, carboxyl, alkoxycarbonyl, halogen, amido, amino or hydroxyl.

The term «A₂ group» is understood to mean a heterocycle defined by dihydrofuranyl, tetrahydrofuranyl, butyrolactoneyl, dihydrothiophenyl, tetrahydrothiophenyl, tetrahydrothiophenoneyl, iminothiolanyl, dihydropyrrolyl, pyrrolidinyl, pyrrolidinoneyl, imidazolidinoneyl, imidazolidinethioneyl, oxazolidinyl, oxazolidinoneyl, oxazolanethioneyl, thiazolidinyl, isothiazoloneyl, mercaptothiazolinyl, pyrazolidinoneyl, iminothiolanyl, dioxolanyl, pentalactoneyl, dioxanyl, dihydropyridinyl, piperidinyl, pentalactamyl, morpholinyl, pyrazoli(di)nyl, pyrimi(di)nyl, pyrazinyl, piperazinyl and azepinyl.

Among these substituents, R₁ preferably represents a hydrogen atom, a methyl, ethyl, isopropyl, allyl, phenyl, benzyl, fluorobenzyl, hydroxybenzyl, difluorobenzyl, trifluorobenzyl, chlorobenzyl, bromobenzyl, methoxybenzyl, dimethoxybenzyl, (trifluoromethoxy)benzyl, 3,4-methylenedioxybenzyl, 6-chloropiperonyl, 4-methylthiobenzyl, 4-methylsulphonylbenzyl, 4-acetylamino benzyl, 4-carboxybenzyl, 1-naphthomethyl or 2-naphthomethyl radical; or a 2-hydroxyethyl, 2-methoxyethyl or 2-ethoxyethyl group.

More preferably still, R₁ represents a hydrogen atom or a

methyl radical.

According to the invention, R_2 preferably denotes a hydrogen atom, an amino group or an A_1 , A_2 , A_3 , A_4 or A_5 group as defined above, optionally separated from the sulphur (in the 8 position) of the sulphonamide functional group of the compound of formula (I) by an -NH- or -N-(C_1 - C_3)alkyl- group.

10 Among these substituents, R_2 preferably denotes a radical chosen from the group (G1) consisting of the methyl, trifluoromethyl, ethyl, 2-chloroethyl, propyl, 3-chloropropyl, isopropyl, butyl, phenyl, ethoxy, amino and dimethylamino radicals.

15 More preferably still, R_2 represents a methyl, ethyl, phenyl or dimethylamino radical.

According to the invention, R_3 and R_4 , which are identical or different, preferably denote a hydrogen or halogen atom; a hydroxyl or amino group; an A_1 , A_4 or A_5 group as defined above; or an A_1 , A_2 , A_3 , A_4 or A_5 group as defined above separated from the phenol nucleus of the formula (I) by an oxygen atom or by an -NH-,
20 -N-(C_1 - C_3)alkyl-, -O(CO)-, -NH(CO)-, -N-(C_1 - C_3)alkyl(CO)-, -NH[C=NH]-, -NH(CO)NH-, -NH(CO)N-(C_1 - C_3)alkyl-,
25 -NH(CO)O-, -NHSO₂-, -NHSO₂NH- or -NHSO₂N-(C_1 - C_3)alkyl-group.

30 Among these substituents, R_3 preferably represents a hydrogen or chlorine atom; a methyl, hydroxymethyl, methoxymethyl, 1-hydroxyethyl, aminomethyl or methyl-

aminomethyl radical; a hydroxyl, methoxy or acetoxy radical; an amino, methylamino or 2-hydroxyethylamino radical; an -NH(CO)R, group in which R, represents one of the radicals listed in the group (G2) consisting of the

5 methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, neopentyl, hexyl; cyclopropyl, cyclobutyl, cyclopentyl, cyclopentylmethyl, 3-cyclopentylpropyl, cyclohexyl, 2-cyclohexylethyl, norbornan-2-yl, vinyl, 1-methylvinyl, 2-methylvinyl, 2,2-dimethyl-

10 vinyl, allyl, 3-butenyl; phenyl, methylphenyl, dimethylphenyl, 2,4,6-trimethylphenyl, 4-ethylphenyl, (trifluoromethyl)phenyl, hydroxyphenyl, methoxyphenyl, ethoxyphenyl, acetoxyphenyl, (trifluoromethoxy)phenyl, aminophenyl, 4-dimethylaminophenyl, fluorophenyl,

15 difluorophenyl, fluoro(trifluoromethyl)phenyl, chlorophenyl, dichlorophenyl, bromophenyl, naphth-1-yl, naphth-2-yl, (2-methoxy)naphth-1-yl, benzyl, 4'-methoxybenzyl, 2',5'-dimethoxybenzyl, 3',4'-dimethoxybenzyl, 4'-fluorobenzyl, 4'-chlorobenzyl,

20 phenethyl, 2-phenylvinyl, (1-naphthyl)methyl, (2-naphthyl)methyl; tetrahydrofuran-2-yl, furan-2-yl, 5-methyl-2-(trifluoromethyl)furan-3-yl, 2-methyl-5-phenylfuran-3-yl, thiophen-2-yl, (thiophen-2-yl)methyl, 3-chlorothiophen-2-yl, 2,5-dichlorothiophen-3-yl,

25 benzothiophen-2-yl, 3-chlorobenzothiophen-2-yl, isoxazol-5-yl, 5-methylisoxazol-3-yl, 3,5-dimethylisoxazol-4-yl, 1,3-dimethylpyrazol-5-yl, 1-ethyl-3-methylpyrazol-5-yl, 1-tert-butyl-3-methylpyrazol-5-yl, 3-tert-butyl-1-methylpyrazol-5-yl, 4-bromo-1-ethyl-3-methylpyrazol-

30 5-yl, indol-3-ylcarboxyl, pyridinyl, chloropyridinyl, dichloropyridinyl, 5-(bromo)pyridin-3-yl, piperazin-2-yl, quinoxal-2-yl; fluoromethyl, difluoromethyl,

trifluoromethyl, 1,1,2,2-tetrafluoroethyl,
 pentafluoroethyl, heptafluoropropyl,
 1,1,2,2,3,3,4,4-octafluorobutyl, nonafluorobutyl, chloro-
 methyl, chloroethyl, 1,1-dimethyl-2-chloroethyl, 1,2-di-
 5 chloroethyl, 1-chloropropyl, 3-chloropropyl, 4-chloro-
 butyl, hydroxymethyl, methoxymethyl, phenoxymethyl,
 (4-chlorophenoxy)methyl, benzyloxymethyl, acetoxymethyl,
 1,2-dihydroxyethyl, 1-phenoxyethyl, 1-acetoxyethyl,
 2-(2-carboxyethoxy)ethyl, 1-phenoxyethyl, 1-acetoxyethyl,
 10 methoxycarbonyl, ethoxycarbonyl, (methoxycarbonyl)methyl,
 2-carboxyethyl, 2-(methoxycarbonyl)ethyl, 2-carboxycyclo-
 propyl, 2-carboxycyclohexane; methoxy, ethoxy, propoxy,
 isopropoxy, butoxy, isobutoxy, pentoxy, neopentoxy,
 hexyloxy, cyclopentyloxy, cyclohexyloxy, vinyloxy,
 15 allyloxy, propargyloxy, chloromethoxy, 1-chloroethoxy,
 2-methoxyethoxy, 4-chlorobutoxy, phenoxy, 4-methyl-
 phenoxy, 4-fluorophenoxy, 4-bromophenoxy, 4-chloro-
 phenoxy, 4-methoxyphenoxy, naphth-2-yloxy, benzyloxy;
 amino, methylamino, ethylamino, propylamino, isopropyl-
 20 amino, butylamino, cyclohexylamino, allylamino, 2-chloro-
 ethylamino, 3-chloropropylamino, carboxymethylamino,
 phenylamino, fluorophenylamino, (trifluoromethyl)phenyl-
 amino, chlorophenylamino, bromophenylamino, 4-acetyl-
 phenylamino, methoxyphenylamino, (trifluoromethoxy)-
 25 phenylamino, naphth-1-ylamino, benzylamino, phenethyl-
 amino, pyrid-3-ylamino, dimethylamino, 1-pyrrolidinyl and
 4-morpholinyl radicals; or an $-NHSO_2R_s$ group in which R_s
 represents one of the radicals listed in the group (G1)
 as defined above.

30

More preferably still, R_s represents a hydrogen atom; a
 methyl, hydroxymethyl, aminomethyl, hydroxyl, methoxy,

amino or methylamino radical; an -NH(CO)R_8 group in which R_8 is chosen from the group (G3) consisting of the methyl, ethyl, propyl, allyl, phenyl, tetrahydrofuran-2-yl, furan-2-yl, thiophen-2-yl, pyridinyl, piperazin-2-yl, fluoromethyl, chloromethyl, 2-chloroethyl, methoxymethyl, acetoxymethyl, 1,2-dihydroxyethyl, methoxycarbonyl, 2-carboxyethyl, methoxy, ethoxy, propoxy, allyloxy, 2-chloroethoxy, 2-methoxyethoxy, amino, ethylamino, allylamino, 2-chloroethylamino, pyridylamino, dimethylamino, 1-pyrrolidinyl and 4-morpholinyl radicals; or a methanesulphonylamino, ethanesulphonylamino, benzene-sulphonylamino or dimethylaminosulphonylamino group.

Among these substituents, R_4 preferably represents a hydrogen or chlorine atom; a methyl, ethyl, hydroxymethyl, methoxymethyl, aminomethyl or methylaminomethyl radical; a hydroxyl, methoxy, acetoxy, amino, methylamino, N-piperidino or N-morpholino group; an -NH(CO)R_{10} group in which R_{10} represents one of the radicals listed in the group (G2) defined above; or an $\text{-NHSO}_2\text{R}_{11}$ group in which R_{11} represents one of the radicals listed in the group (G1) defined above.

More preferably still, R_4 represents a hydrogen or chlorine atom; a methyl, hydroxymethyl, aminomethyl, hydroxyl, methoxy, amino or methylamino radical; an -NH(CO)R_{12} group in which R_{12} represents one of the radicals listed in the group (G3) defined above; or a methanesulphonylamino, ethanesulphonylamino, benzene-sulphonylamino or dimethylaminosulphonylamino group.

According to the invention, R_5 is preferably chosen from

a hydrogen or halogen atom; an A_1 , A_4 or A_5 group as defined above; or an A_1 , A_2 , A_3 , A_4 or A_5 group as defined above separated from the phenyl nucleus of the compounds of formula (I) by an oxygen or sulphur atom or by an
5 -NH-, -N-(C_1 - C_3)alkyl-, -NH(CO)-, -N-(C_1 - C_3)alkyl(CO)-, -NH[C=NH]-, -NH(CO)NH-, -NH(CO)N-(C_1 - C_3)alkyl- or -NH(CO)O- group.

Among these substituents, R_2 preferably represents a
10 hydrogen, chlorine, fluorine or bromine atom; a methyl, trifluoromethyl, allyl, hydroxymethyl, methoxymethyl, 1-hydroxyethyl, aminomethyl, methylaminomethyl, methoxy, acetoxy or methylamino radical; an -NH(CO) R_{13} group in which R_{13} represents one of the radicals listed in the
15 group (G2) defined above; or an -NHSO₂ R_{14} group in which R_{14} represents one of the radicals listed in the group (G1) defined above.

More preferably still, R_2 represents a hydrogen, chlorine
20 or fluorine atom; a methyl, hydroxymethyl, aminomethyl, methoxy or methylamino group; an -NH(CO) R_{15} group in which R_{15} represents one of the radicals listed in the group (G3) defined above; or a methanesulphonylamino, ethane-sulphonylamino, benzenesulphonylamino or dimethylamino-
25 sulphonylamino group.

According to the invention, Y is preferably chosen from a hydrogen, chlorine, fluorine or bromine atom; a methoxy, ethoxy, propoxy, benzyloxy or phenoxy group; or
30 an -OCH₂CH₂OCH₃, -OCH₂CH₂OCH₃, -OCH₂CH₂N(CH₃)₂, -OCH₂(CO)OH, -OCH₂(CO)OCH₃, -OCH₂(CO)OC₂H₅, -SCH₂CH₂CO₂H or -NHSO₂CH₃ group.

More preferably still, Y is chosen from a hydrogen or chlorine atom or a methoxy, $-\text{OCH}_2(\text{CO})\text{OH}$ or $-\text{OCH}_2(\text{CO})\text{OCH}_3$ group.

5

Among the compounds of formula (I), preference is particularly given to those in which:

- i) - R_1 represents a hydrogen atom;
- R_2 represents a methyl, ethyl, phenyl or dimethylamino radical;
10 - R_3 represents a hydroxyl, amino or methylamino radical; an $-\text{NH}(\text{CO})\text{R}_{16}$ group in which R_{16} represents a radical chosen from the group (G4) consisting of the methyl, methoxymethyl, 2-carboxyethyl, methoxy, amino, ethylamino and 1-pyrrolidinyl radicals; methanesulphonyl-
15 amino, ethanesulphonylamino and dimethylaminosulphonyl-amino;
- R_4 represents a hydrogen or chlorine atom or a methyl group;
20 - R_5 represents a hydrogen, chlorine or fluorine atom or a methyl group;
- Y represents a hydrogen or chlorine atom or a methoxy or $-\text{OCH}_2(\text{CO})\text{OCH}_3$ group;
- 25 ii) - R_1 represents a hydrogen atom;
- R_2 represents a methyl, ethyl, phenyl or dimethyl-amino radical;
- R_3 represents a hydrogen atom or a methyl radical;
- R_4 represents a hydroxyl, amino, methylamino or
30 $-\text{NH}(\text{CO})\text{R}_{17}$ group in which R_{17} represents one of the radicals listed in the group (G4) defined above; or a methanesulphonylamino, ethanesulphonylamino or dimethyl-

aminosulphonylamino group;

- R_2 represents a hydrogen, chlorine or fluorine atom or a methyl, methoxy or methylamino group;
- Y represents a hydrogen or chlorine atom or a methoxy or $-OCH_2(CO)OCH_3$ group;

iii) - R_1 represents a hydrogen atom;

- R_2 represents a methyl, ethyl, phenyl or dimethylamino radical;
 - 10 - R_3 represents a hydrogen atom or a methyl radical;
 - R_4 represents a hydrogen or chlorine atom or a methyl, methoxy or methylamino radical;
 - R_5 represents a methylamino or $-NH(CO)R_{12}$ group in which R_{12} represents one of the radicals listed in the group (G4) defined above; or a methanesulphonylamino, ethanesulphonylamino or dimethylaminosulphonylamino group;
 - 15 - Y represents a hydrogen or chlorine atom or a methoxy or $-OCH_2(CO)OCH_3$ group;
- 20
- iv) - R_1 represents a hydrogen atom;
- R_2 represents a methyl, ethyl, phenyl or dimethylamino radical;
 - R_3 represents a hydrogen atom or a methyl radical;
 - 25 - R_4 represents a hydrogen or chlorine atom or a methyl radical;
 - R_5 represents a hydrogen, chlorine or fluorine atom or a methyl radical;
 - Y represents a hydrogen or chlorine atom or a methoxy or $-OCH_2(CO)OCH_3$ group.
- 30

Mention may be made, among the compounds of formula (I)

above, of:

- N-(2-hydroxyphenyl)methanesulphonamide;
- N-(2-hydroxy-4-methylphenyl)methanesulphonamide;
- N-(2-hydroxy-4-aminophenyl)methanesulphonamide;
- 5 - N-(2-hydroxy-4-(acetylamino)phenyl)methane-sulphonamide;
- N-(2-hydroxy-4-(methoxycarbonylamino)phenyl)methane-sulphonamide;
- N-(2-hydroxy-5-chlorophenyl)methanesulphonamide;
- 10 - N-(2-hydroxy-4-methyl-5-chlorophenyl)methane-sulphonamide;
- N-(2-hydroxy-4-amino-5-chlorophenyl)methane-sulphonamide;
- N-(2-hydroxy-4-acetylamino-5-chlorophenyl)methane-sulphonamide;
- 15 - N-(2-hydroxy-4-methoxycarbonylamino-5-chlorophenyl)-methanesulphonamide;
- N-(2-hydroxy-5-methoxyphenyl)methanesulphonamide;
- N-(2-hydroxy-4-methyl-5-methoxyphenyl)methane-sulphonamide;
- 20 - N-(2-hydroxy-4-amino-5-methoxyphenyl)methane-sulphonamide;
- N-(2-hydroxy-4-acetylamino-5-methoxyphenyl)methane-sulphonamide;
- 25 - N-(2-hydroxy-4-methoxycarbonylamino-5-methoxyphenyl)-methanesulphonamide;
- N-(2-hydroxy-6-aminophenyl)methanesulphonamide;
- N-(2-hydroxy-6-(acetylamino)phenyl)methane-sulphonamide;
- 30 - N-(2-hydroxy-4,6-diaminophenyl)methanesulphonamide;
- N-(2-hydroxy-4-acetylamino-6-aminophenyl)methane-sulphonamide;

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- N-(2-hydroxy-3,5-dichloro-4-methylphenyl)methane-sulphonamide;
- N-(2-hydroxy-3,5-dichloro-4-aminophenyl)methane-sulphonamide;
- 5 - N-(2-hydroxy-3,5-dichloro-4-(acetylamino)phenyl)-methanesulphonamide;
- N-(2-hydroxy-3,5-dichloro-4-(methoxycarbonylamino)-phenyl)methanesulphonamide;
- N-(2-hydroxy-3-(methanesulphonylamino)phenyl)methane-
- 10 sulphonamide;
- N-(2-hydroxyphenyl)benzenesulphonamide;
- N-(2-hydroxy-4-methylphenyl)benzenesulphonamide;
- N-(2-hydroxy-4-aminophenyl)benzenesulphonamide;
- N-(2-hydroxy-4-(acetylamino)phenyl)benzene-
- 15 sulphonamide;
- N-(2-hydroxy-4-(methoxycarbonylamino)phenyl)benzene-sulphonamide;
- N-(2-hydroxy-5-chlorophenyl)benzenesulphonamide;
- N-(2-hydroxy-4-methyl-5-chlorophenyl)benzene-
- 20 sulphonamide;
- N-(2-hydroxy-4-amino-5-chlorophenyl)benzene-sulphonamide;
- N-(2-hydroxy-4-acetylamino-5-chlorophenyl)benzene-sulphonamide;
- 25 - N-(2-hydroxy-4-methoxycarbonylamino-5-chlorophenyl)-benzenesulphonamide;
- N-(2-hydroxy-5-methoxyphenyl)benzenesulphonamide;
- N-(2-hydroxy-4-methyl-5-methoxyphenyl)benzene-sulphonamide;
- 30 - N-(2-hydroxy-4-amino-5-methoxyphenyl)benzene-sulphonamide;
- N-(2-hydroxy-4-acetylamino-5-methoxyphenyl)benzene-

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- 5
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- and their addition salts with an acid.
- 5 - N-(2-hydroxy-6-(acetyl-amino)phenyl)benzene-sulphonamide;
 - N-(2-hydroxy-4,6-diaminophenyl)benzenesulphonamide;
 - N-(2-hydroxy-4-acetyl-amino-6-aminophenyl)benzene-sulphonamide;
 - 10 - N-(2-hydroxy-3,5-dichloro-4-methylphenyl)benzene-sulphonamide;
 - N-(2-hydroxy-3,5-dichloro-4-aminophenyl)benzene-sulphonamide;
 - 15 - N-(2-hydroxy-3,5-dichloro-4-(acetyl-amino)phenyl)benzenesulphonamide;
 - N-(2-hydroxy-3,5-dichloro-4-(methoxycarbonylamino)-phenyl)benzenesulphonamide;
 - N-(2-hydroxy-3-(benzenesulphonylamino)phenyl)benzene-sulphonamide;

25 The compounds of formula (I) in accordance with the invention can be prepared according to methods well known in the state of the art and disclosed, for example, in Patent Applications or Patents EP 0 718 277, EP 0 576 172, US 4 250 246, DE 2 906 526, US 4 200 466, US 4 004 028, US 3 920 444, DE 2 156 480 and US 3 660 487.

30 The compound or compounds of formula (I) in accordance with the invention and/or the addition salt or their addition salts with an acid preferably represent from

0.0005 to 12% by weight approximately of the total weight of the dyeing composition and more preferably still from 0.005 to 6% by weight approximately of this weight.

- 5 The oxidation dyeing composition according to the invention comprises one or more oxidation bases which are preferably chosen from the oxidation bases conventionally used in oxidation dyeing and among which may in particular be mentioned para-phenylenediamines, bisphenyl-
10 alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases.

Mention may more particularly be made, among the para-phenylenediamines, by way of example, of para-
15 phenylenediamine, para-toluylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-
20 phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β -hydroxyethyl)-amino-2-methylaniline, 4-N,N-bis(β -hydroxyethyl)amino-2-chloroaniline, 2- β -hydroxyethyl-para-phenylenediamine,
25 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl, β -hydroxyethyl)-para-phenylenediamine, N-(β,β -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-
30 phenylenediamine, N-phenyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2- β -acetyl-

aminoethyloxy-para-phenylenediamine, N-(β -methoxyethyl)-para-phenylenediamine and their addition salts with an acid.

5 Preference is very particularly given, among the para-phenylenediamines mentioned above, to para-phenylenediamine, para-toluylenediamine, 2-isopropyl-para-phenylenediamine, 2- β -hydroxyethyl-para-phenylene-
10 diamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine, 2- β -acetylaminioethyloxy-para-phenylenediamine and their addition salts with an acid.

15 Mention may more particularly be made, among the bis-phenylalkylenediamines, by way of example, of N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-amino-
20 phenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β -hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-(methyl)aminophenyl)tetramethylenediamine, N,N'-diethyl-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine,
25 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane and their addition salts with an acid.

Mention may more particularly be made, among the para-aminophenols, by way of example, of para-aminophenol,
30 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-(hydroxymethyl)phenol, 4-amino-2-methylphenol, 4-amino-2-(hydroxymethyl)phenol, 4-amino-2-(methoxymethyl)phenol,

4-amino-2-(aminomethyl)phenol, 4-amino-2-[(β -hydroxyethyl)aminomethyl]phenol, 4-amino-2-fluorophenol and their addition salts with an acid.

5 Mention may more particularly be made, among the ortho-aminophenols, by way of example, of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-aminophenol and their addition salts with an acid.

10

Mention may more particularly be made, among the heterocyclic bases, by way of example, of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

15

Mention may more particularly be made, among the pyridine derivatives, of the compounds disclosed, for example, in Patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-amino-

20 pyridine, 2,3-diamino-6-methoxypyridine, 2-(β -methoxyethyl)amino-3-amino-6-methoxypyridine, 3,4-diaminopyridine and their addition salts with an acid.

Mention may more particularly be made, among the
25 pyrimidine derivatives, of the compounds disclosed, for example, in German Patent DE 2 359 399 or Japanese Patents JP 88-169 571 and JP 91-10659 or Patent Application WO 96/15765, such as 2,4,5,6-tetraamino-pyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine,
30 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine or 2,5,6-triaminopyrimidine.

Mention may more particularly be made, among the pyrazole derivatives, of the compounds disclosed in Patents DE 3 843 892 and DE 4 133 957 and Patent Applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and

5 DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)-pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole,

10 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-(hydroxymethyl)pyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-

15 3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-(methylamino)pyrazole, 3,5-diamino-4(β -hydroxyethyl)amino-1-methylpyrazole and their addition salts with an acid.

20

The oxidation base or bases preferably represent from

25 0.0005 to 12% by weight approximately of the total weight of the dyeing composition and more preferably still from 0.005 to 6% by weight approximately of this weight.

The dyeing composition in accordance with the invention

30 can also include, in addition to the compound or compounds of formula (I) above, one or more additional couplers which can be chosen from the couplers conven-

tionally used in oxidation dyeing and among which may in particular be mentioned meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers, such as, for example, indole derivatives, indoline
5 derivatives, pyridine derivatives and pyrazolones, and their addition salts with an acid.

These couplers are chosen more particularly from 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-
10 2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β -hydroxyethyloxy)benzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane,
15 sesamol, β -naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-5-one and their addition salts with an acid.

20

When they are present, these additional couplers preferably represent from 0.0001 to 10% by weight approximately of the total weight of the dyeing composition and more preferably still from 0.005 to 5% by weight approximately
25 of this weight.

Generally, the addition salts with an acid which can be used in the context of the dyeing compositions of the invention (compounds of formula (I), oxidation bases and
30 additional couplers) are chosen in particular from hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates and acetates.

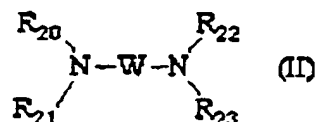
The medium appropriate for dyeing (or vehicle) is generally composed of water or of a mixture of water and of at least one organic solvent, in order to dissolve the compounds which would not be sufficiently soluble in water. Mention may be made, for example, as organic solvent, of lower C₁-C₄ alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers, such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monomethyl ether; and aromatic alcohols such as benzyl alcohol or phenoxyethanol, the analogous products and their mixtures.

The solvents can be present in proportions preferably of between 1 and 40% by weight approximately with respect to the total weight of the dyeing composition and more preferably still between 5 and 30% by weight approximately.

The pH of the dyeing composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 11 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents commonly used in dyeing keratinous fibres.

Mention may be made, among acidifying agents, by way of example, of inorganic or organic acids, such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, such as acetic acid, tartaric acid, citric acid or lactic acid, or sulphonc acids.

Mention may be made, among basifying agents, by way of example, of aqueous ammonia, alkaline carbonates, alkanolamines, such as mono-, di- and triethanolamines, and
5 their derivatives, sodium hydroxide, potassium hydroxide



and the compounds of following formula (II):
in which W is a propylene residue which is or is not substituted by a hydroxyl group or a C₁-C₆ alkyl radical and R₂₀, R₂₁, R₂₂ and R₂₃, which are identical or different,
10 represent a hydrogen atom or a C₁-C₆ alkyl or C₁-C₆ hydroxyalkyl radical.

The oxidation dyeing compositions in accordance with the invention can also include at least one direct dye, in
15 particular for modifying the shades or enriching them with highlights.

The dyeing composition in accordance with the invention can also include various adjuvants conventionally used in
20 hair dyeing compositions, such as anionic, cationic, nonionic, amphoteric or zwitterionic surface-active agents or their mixtures, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or their mixtures, inorganic or organic thickening agents, antioxidizing
25 agents, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioning agents, such as, for example, volatile or non-volatile and modified or unmodified silicones, film-forming

agents, ceramides, preserving agents or opacifying agents.

Of course, a person skilled in the art will take care to
5 choose this or these optional additional compound or
compounds so that the advantageous properties intrin-
sically attached to the oxidation dyeing composition in
accordance with the invention are not, or not
substantially, detrimentally affected by the envisaged
10 addition or additions.

The dyeing composition according to the invention can be
provided in various forms, such as in the form of
liquids, creams or gels or in any other form appropriate
15 for carrying out dyeing of keratinous fibres and in
particular human hair.

Another subject-matter of the invention is a process for
the oxidation dyeing of keratinous fibres and in
particular human keratinous fibres, such as the hair,
20 employing the dyeing composition as defined above.

According to this process, at least one dyeing
composition as defined above is applied to the fibres,
the colour being developed at acidic, neutral or alkaline
25 pH using an oxidizing agent which is added only at the
time of use to the dyeing composition or which is present
in an oxidizing composition applied simultaneously or
sequentially.

30 According to a preferred embodiment of the dyeing process
of the invention, the dyeing composition described above
is preferably mixed, at the time of use, with an oxidiz-

ing composition comprising, in a medium appropriate for dyeing, at least one oxidizing agent present in an amount sufficient to develop a colouring. The mixture obtained is subsequently applied to the keratinous fibres and is
5 left to stand for 3 to 50 minutes approximately, preferably 5 to 30 minutes approximately, after which the hair is rinsed, washed with shampoo, rinsed again and dried.

10 The oxidizing agent can be chosen from oxidizing agents conventionally used for the oxidation dyeing of keratinous fibres and among which may be mentioned hydrogen peroxide, urea hydrogen peroxide, alkali metal bromates, persalts, such as perborates and persulphates,
15 and enzymes, such as peroxidases, laccases, tyrosinases and oxidoreductases, among which may in particular be mentioned pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

20 The pH of the oxidizing composition including the oxidizing agent as defined above is such that, after mixing with the dyeing composition, the pH of the resulting composition applied to keratinous fibres
25 preferably varies between 3 and 12 approximately and more preferably still between 5 and 11. It is adjusted to the desired value by means of acidifying or basifying agents commonly used in dyeing keratinous fibres and as defined above.

30 The oxidizing composition as defined above can also include various adjuvants conventionally used in hair

dyeing compositions and as defined above.

The composition which is finally applied to keratinous fibres can be provided in various forms, such as in the form of liquids, creams or gels or in any other form appropriate for carrying out dyeing of keratinous fibres and in particular of human hair.

A final subject-matter of the invention is a multi-compartment device or dyeing kit or any other packaging system with several compartments, a first compartment of which includes the dyeing composition as defined above and a second compartment of which includes the oxidizing composition as defined above. These devices can be equipped with a means allowing the desired mixture to be delivered to the hair, such as the devices disclosed in Patent FR-2 586 913 on behalf of the Applicant Company.

The examples which follow are intended to illustrate the invention without, however, limiting the scope thereof.

EXAMPLES

Each of the tests described in detail below corresponds to the use of the following bases 1 to 5 and of the following couplers 1 to 4 of the 2-(sulphonylamino)phenol type of formula (I):

Coupler 1: N-(2-hydroxy-4-methylphenyl)methanesulphonamide;

Coupler 2: N-(4-amino-2-hydroxyphenyl)methanesulphonamide;

Coupler 3: N-(4-amino-2-hydroxyphenyl)benzenesulphonamide;

Coupler 4:N-(2-hydroxy-4-methylphenyl)benzene-sulphonamide.

- Base 1: para-phenylenediamine;
 5 Base 2: para-aminophenol;
 Base 3: 4,5-diamino-1-ethyl-3-methylpyrazole-2HCl;
 Base 4: 3,7-diaminopyrazolo[1,5-a]pyrimidine-2HCl;
 Base 5: N,N-bis(hydroxyethyl)-para-phenylenediamine sulphate.

10

Dyeing compositions are prepared from these bases and couplers, which compositions comprise (content in grams):

Coupler	(*)
Base	(*)
Alkyl (C ₈ /C ₁₀ 50/50) polyglucoside as a buffered 60% aqueous solution	5.4 g
Ethyl alcohol, 96°, denatured	18 g
Benzyl alcohol	1.8 g
Polyethylene glycol (8 EO)	2.7 g
Diethylenetriaminepentaacetic acid, pentasodium salt, as a 40% aqueous solution	1.08 g
Sodium metabisulphite powder	0.585 g
Aqueous ammonia	10 g
Demineralized water	q.s. for 100 g

15 (*) the amounts of coupler and of base used are shown in

the tables below:

Examples	1	2	3	4	5
Coupler 1	0.603 g	0.603 g	0.603 g	0.603 g	0.603 g
Base 1	0.32 g	-	-	-	-
Base 2	-	0.33 g	-	-	-
Base 3	-	-	0.63 g	-	-
Base 4	-	-	-	0.66 g	-
Base 5	-	-	-	-	0.89 g

Examples	6	7	8	9	10
Coupler 2	0.89 g	0.89 g	0.89 g	0.89 g	0.89 g
Base 1	0.32 g	-	-	-	-
Base 2	-	0.33 g	-	-	-
Base 3	-	-	0.63 g	-	-
Base 4	-	-	-	0.66 g	-
Base 5	-	-	-	-	0.89 g

Examples	11	12	13	14	15
Coupler 3	0.79 g	0.79 g	0.79 g	0.79 g	0.79 g
Base 1	0.32 g	-	-	-	-
Base 2	-	0.33 g	-	-	-
Base 3	-	-	0.63 g	-	-

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Base 4	-	-	0.66 g	-
Base 5	-	-	-	0.89 g

Examples	16	17	18	19	20
Coupler 4	0.78 g	0.78 g	0.78 g	0.78 g	0.78 g
Base 1	0.32 g	-	-	-	-
Base 2	-	0.33 g	-	-	-
Base 3	-	-	0.63 g	-	-
Base 4	-	-	-	0.66 g	-
Base 5	-	-	-	-	0.89 g

Each of the dyeing compositions thus obtained was mixed with an equal amount of an oxidizing composition consisting of a 20-volume hydrogen peroxide solution (6% by weight) exhibiting a pH of approximately 3.

Each mixture thus obtained exhibited a pH of approximately 9.5 and was applied for 30 minutes to locks of natural grey hair comprising 90% white hairs. The locks of hair were subsequently rinsed, washed with a standard shampoo and then dried.

The level of tone and the highlights of the colouring obtained were subsequently determined. The following results are then obtained:

Examples	Coupler	Base	Highlights and level of tone
1	Coupler 1	Base 1	Ash dark blond
2		Base 2	Ash golden very light blond
3		Base 3	Ash iridescent very light blond
4		Base 4	Deep purple dark blond
5		Base 5	Blueish green blond
6	Coupler 2	Base 1	Ash mahogany dark blond
7		Base 2	Ash golden very light blond
8		Base 3	Ash red dark blond
9		Base 4	Pearlescent ash very light blond
10		Base 5	Intense ash light chestnut
11	Coupler 3	Base 1	Pearlescent mahogany dark blond
12		Base 2	Ash pearlescent coppery blond
13		Base 3	Red pearlescent blond
14		Base 4	Red mahogany dark blond
15		Base 5	Matt blue ash blond
16	Coupler 4	Base 1	Matt ash dark blond
17		Base 2	Pearlescent golden blond
18		Base 3	Ash mahogany very light blond
19		Base 4	Deep purple light chestnut
20		Base 5	Blueish green light chestnut

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